

The University of Chicago

THE REARRANGEMENT
OF CAMPHENE HYDROBROMIDE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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By
LINDSEY MAURICE HOBBS

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To Dr. F. R. Mayo the writer expresses his appreciation for his helpful discussions and criticisms of the work.

INTRODUCTION

In 1922, Meerwein and van Emster published a report¹ on the preparation and determination of camphene hydrochloride and on the factors influencing its rate of rearrangement to the isomeric bornyl and isobornyl chlorides. Later, in 1927, Meerwein extended this study to include camphene hydrobromide² and other esters of camphene hydrate. He found that in both cases, the halogen acid had a marked catalytic influence on the rate of rearrangement of the camphene hydrohalide.

Owing to the sensitivity of hydrogen bromide, in its non-ionic reactions, to the presence of peroxides, a method is indicated by which light may be thrown on the catalytic rôle of hydrogen bromide in the rearrangement of camphene hydrobromide. The present work consists, therefore, of a study of the effect of the presence of oxygen and peroxides on the addition of hydrogen bromide to camphene and on the rate of rearrangement of the resulting camphene hydrobromide.

The presence of an atmosphere of oxygen above the reaction mixture has not been found to produce an effect on the rate of rearrangement unless the reaction mixture contains free hydrogen bromide and an oxygen-carrier, such as an aldehyde. The presence of peroxides in the reaction mixture increases both the rate of addition of hydrogen bromide and the rate of rearrangement of camphene hydrobromide.

The presence of peroxides has not been found to influence the similar reactions involving camphene and hydrogen chloride.

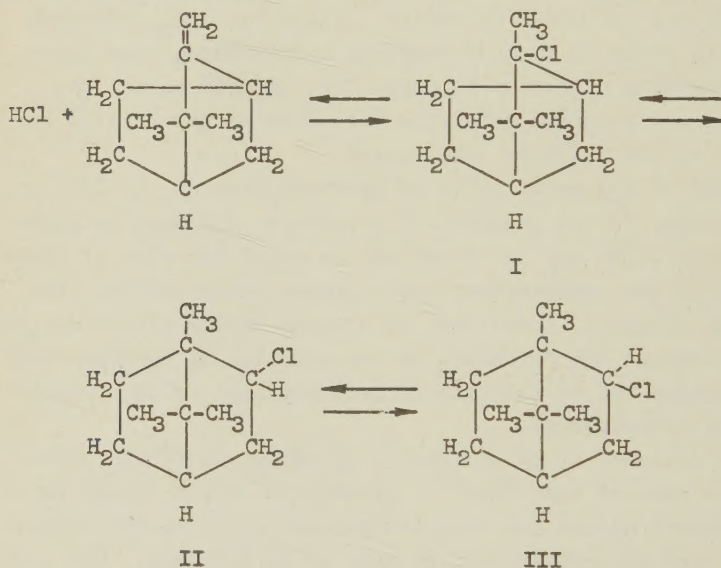
The two papers by Meerwein may well be regarded as classics in terpene chemistry. They form the basis of the present study and will be summarized along with the recent work of Bartlett and Pöckel in the following pages.

¹Meerwein and van Emster, Ber., **55**, 2500-28 (1922).

²Meerwein, Ann. **453**, 16-47 (1927).

PREVIOUS WORK

In his first article Meerwein showed the existence of an equilibrium between the isomeric compounds: camphene hydrochloride (I), isobornyl chloride (II), and bornyl chloride (III). Camphene hydrochloride, further, was found to dissociate into camphene and free hydrogen chloride so that the final equilibrium may be represented:



The rearrangement of camphene hydrochloride into isobornyl chloride takes place in most solvents at a conveniently measurable rate at room temperature or slightly above, while that of isobornyl chloride to bornyl chloride is very slow, usually requiring months. The degree of dissociation of camphene hydrochloride into camphene and hydrogen chloride was found to be subject to catalytic influences, and to vary with temperature and the nature of the medium, but was usually of the order of 5 to 15 per cent of the camphene hydrochloride present.

In seeking the mechanism for these displacements Meerwein made an exhaustive study of the rate of rearrangement of camphene hydrochloride into isobornyl chloride. He made comparisons of the rates of rearrangement in a number of solvents and in the

presence of various anhydrous metallic halides. His findings are enumerated in the following paragraphs.

1. Hydrogen chloride is a catalyst for the rearrangement.
2. There is a rough proportionality between the rate of rearrangement and the dielectric constant of the solvent. The same is also true for the alcoholysis of camphene hydrochloride in different media. Liquid sulfur dioxide, cresol, anisole, and ether as solvents for the rearrangement, are, however, marked exceptions. In the first three, the rearrangement is much more rapid, and in ether much slower, than would be predicted from their dielectric constants.

3. There is no direct connection between the degree of dissociation of camphene hydrochloride into camphene and hydrogen chloride in a given solvent and the rearrangement velocity. In ether, for example, in which the rearrangement is very slow, the degree of dissociation is greatest.

4. The anhydrous metallic chlorides, SbCl_5 , SnCl_4 , FeCl_3 , HgCl_2 , and SbCl_3 , decreasing in the order listed, are strong catalysts for the rearrangement while PCl_5 and SiCl_4 are not.

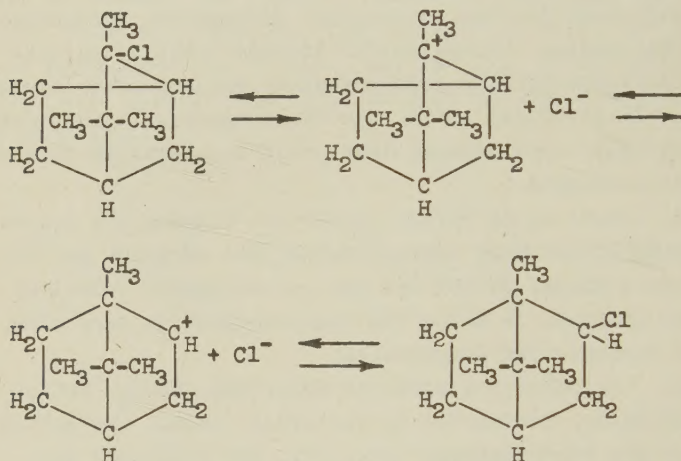
5. The rearrangement was found to be approximately first order. The rate constants calculated on this basis, however, drift (become smaller) as the reaction proceeds. When the reaction was carried out in the presence of one of the metallic chlorides, as SnCl_4 , the rearrangement obeyed first order kinetics throughout.

6. From the fact that 0.2 M HCl in ether was without effect, the authors made the statement that the influence of the catalyst is dependent on the surrounding medium.

In interpreting these data Meerwein ingeniously saw and verified a parallelism between the influence of these solvents and catalysts on both this rearrangement and on the formation of colored solutions of triphenyl methyl chloride. In solvents, such as sulfur dioxide and cresol, which form colored solutions of triphenyl methyl chloride, the rearrangement takes place most rapidly. Ether, which decolorizes solutions of triphenyl methyl chloride, allows the rearrangement to proceed most slowly. The parallelism is borne out in the effect of the metallic chlorides on solutions of triphenyl methyl chloride. Colored solutions are formed in the presence of only those chlorides which have a catalytic effect on the rearrangement. Phosphorus pentachloride and

SiCl_4 are without activity in either case.

Meerwein concluded that the rearrangement proceed by the ionization of camphene hydrochloride followed by an atomic shift in the resulting positive ion. This is represented by the following equations:



They have summarized their data by stating that any material, as solvent or added substance, which enhances the ionization of camphene hydrochloride is a catalyst for the rearrangement.

In the second article referred to above, Meerwein made a report on the rate of rearrangement of other esters of camphene hydrate into the corresponding esters of isoborneol. The rates of rearrangement of the esters of 2-chloro-cymene-5-sulfonic, hydrobromic, hydrochloric, trichloroacetic, and m-nitro-benzoic acids¹ were compared. It was found that the rate of rearrangement of the ester was directly proportional to the strength of its corresponding acid. The effect of solvent and the effect of the presence of metallic chlorides on the rates of rearrangement were found to be completely analogous to those described for camphene hydrochloride. Concerning the catalytic effect of the metallic chlorides an interesting experiment from the work of Hantzsch² was cited. A halogen acid at sufficient dilution in ether pro-

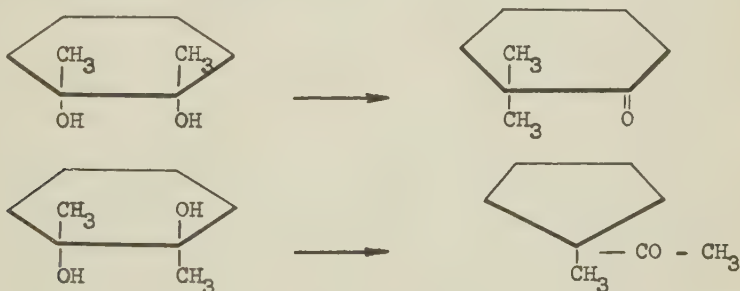
¹These acids are listed in the order of decreasing acid strength.

²Hantzsch, Ber., 58, 631 (1925).

duces the yellow form of dimethylaminoazobenzene. In a separate ether solution, SbCl_5 also produces the yellow form of the indicator. When, however, the two yellow solutions are mixed the red, acid form of the indicator is produced.

Meerwein summarized his findings by stating that the ease with which the esters of camphene hydrate rearrange is roughly directly proportional to the dielectric constant of the medium and depends directly on the strength of the corresponding acid. He re-emphasizes his earlier statement by saying that all substances capable of combining with the acid complex of the ester to form a stronger acid complex, catalyze the rearrangement.

Bartlett and Pöckel¹ have attempted to correlate the mechanism for the rearrangement of camphene hydrochloride with that of replacement reactions² in which a Walden inversion is supposed to take place at every replacement. They found that the cis and trans forms of 1,2-dimethylcyclohexanediol-1,2³ gave different products by boiling in 20 per cent sulfuric acid. The cis form yielded 2,2-dimethylcyclohexanone while the trans form yielded 1-methyl, 1-acetylcyclopentane.



From these results they reasoned that the group which migrates is the one situated near the back side of the carbon atom which loses the hydroxyl group. They felt that since the cis and trans modifications give different products the process of losing the hydroxyl group as the first step leaving an easily racemizable positive carbon atom is excluded.

¹Bartlett and Pöckel, J. Am. Chem. Soc., **59**, 820-25(1937).

²Olson and Long, J. Am. Chem. Soc., **56**, 1294 (1934); Hughes, Juliusburger, Masterman, Topley, and Weiss, J. Chem. Soc., 1525 (1935).

³The identity of the two forms is fairly well established, while final proof awaits the resolution of the two transforms.

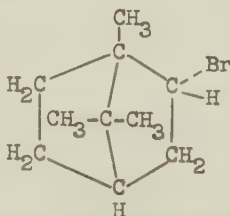
These authors assumed by analogy that camphene hydrochloride has the cis configuration, i.e., its chlorine atom is situated in space adjacent to the single carbon bridge. On this basis they assumed that the rearrangement of camphene hydrochloride and that of dimethylcyclohexanediols are of the same type.

In a later paper¹ they made a report of a kinetic study of the rearrangement of camphene hydrochloride in nitrobenzene. They found the rate of rearrangement to be proportional to the first power of the camphene hydrochloride and to the first power of the free hydrogen chloride concentrations. Owing to the equilibrium between camphene hydrochloride, camphene and hydrogen chloride, the order of the rearrangement was found to be $3/2$ when the concentrations of camphene and hydrogen chloride were equal. In the presence of excess camphene the rearrangement was second-order with respect to camphene hydrochloride, and in the presence of excess hydrogen chloride it was first order.

Chloride ion from lithium chloride in acetone as the solvent was not found to have a catalytic effect. The presence of o-cresol, in a comparatively large amount in proportion to the quantity of camphene hydrochloride, produced a strong acceleration on the reaction rate. This catalytic effect of o-cresol was apparently independent of the catalytic effect of free hydrogen chloride.

Thus these authors have concluded that the rearrangement is not a spontaneous, unimolecular regrouping as Meerwein suggested. They have shown that the rate of rearrangement is dependent on the concentration of hydrogen chloride and have concluded that it would not take place in the absence of hydrogen chloride.

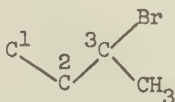
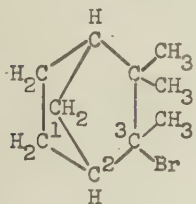
The structures of these terpene derivatives have not been established. There is some evidence that isobornyl bromide is the exo form,² i.e., the bromine atom is situated in space trans to the isopropyl bridge.



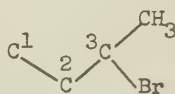
¹Bartlett and Pockel, J. Am. Chem. Soc., **60**, 1585-90 (1938).

²Asahina, Ishidate, and Sano, Ber., **69**, 343 (1936).

The spatial configuration of the atoms of camphene hydrobromide involved in the rearrangement is represented by one or the other of the following diagrams:



I



II

The diastereoisomeric methyl camphenilyl bromide has not been prepared or at least its existence has not been recognized.

The rearrangement is assumed to take place by the breaking of the bond between carbon atoms 1 and 2, followed by the formation of a bond between carbon atoms 1 and 3. During this process the bromine atom is lost from carbon 3, and one becomes attached to carbon 2.

Meerwein's mechanism applies equally well to either of the structures represented. Accordingly, by his mechanism it would be predicted that camphene hydrobromide and methyl camphenilyl bromide would rearrange to isobornyl bromide with equal ease.

The suggestions of Bartlett and Pöckel can be applied only to the structure indicated by the diagram II. Accordingly, methyl camphenilyl bromide would not be expected to rearrange unless the rearrangement is preceded by racemization. The existence of the latter process in the rearrangement is explicitly denied by Bartlett and Pöckel.

PRESENTATION OF DATA

The Rate of Rearrangement of Camphene Hydrobromide

From the previous work it is clear that the mechanism of the rearrangement is complex and that the rate of rearrangement should be very sensitive to the presence of hydrogen bromide. In order to obtain comparable results an apparatus (described in the Experimental Part) was designed by which the rate of rearrangement could be followed under an inert atmosphere and in the presence of definite amounts of hydrogen bromide in the reaction mixture.

Determinations were made at the different times for free

hydrogen bromide and for that which is here indicated as "total active bromide." The latter figure represents the sum of the value of camphene hydrobromide and hydrogen bromide. Thus the value for camphene hydrobromide is obtained by subtracting the value found for free hydrogen bromide from that for the total active bromide.

Ligroin free of peroxides and unsaturated compounds was used throughout as the solvent. The volume of the reaction mixtures was always 100 cc. and the concentrations are given in millimols per 100 cc. The molarity of the solutions is one hundredth of the concentrations given.

The experiments were carried out at 0°C. and 25°C.

The mixing of hydrogen bromide with camphene was performed in vacuo at the temperature of liquid nitrogen. The reaction mixture was then warmed as rapidly as possible to the specified temperature. Since some rearrangement occurred before the given temperature was reached, initial values of the concentrations of the reactants are given in Table 1 for the assumed zero-time. These values have been obtained by extrapolating to the assumed zero-time the best straight-line function of the concentration of the total active bromide (TABr) and that of camphene hydrobromide (C. HBr) versus time. The initial value of the hydrogen bromide was then determined by difference. These values are indicated in Table 1 with the superscript zero. The functions of the concentrations C. HBr and TABr which were plotted against time for the purpose of extrapolation were $\log C$, $1/C$, and $1/c^2$. For those experiments for which no straight-line function of the concentrations expressing the initial rate was found, one hundred per cent addition of the hydrogen bromide is assumed. This assumption is indicated by "(100)" in Table 1 under "% addition." Thus the initial concentration of camphene hydrobromide for these experiments is assumed to be the concentration of the camphene added.

The presence of different catalysts in the reaction mixture and the presence of different initial concentrations of hydrogen bromide produce in each case a different kinetic picture. The kinetic relationship between the concentrations of the reactants in the presence of different catalysts has not been found. For the purpose of comparison, however, plots were made for each experiment for the type reactions of the first-, second-, and third-order with respect to camphene hydrobromide. Where an ap-

TABLE I

SUMMARY OF DATA ON THE RATE OF REARRANGEMENT OF CAMPHENE HYDROBROMIDE

Expt. No.	Camphene mM	HBr M%	Catalyst Added	Temp. Deg. C.	C. HBr°	TABr°	% Free HBr	% Add'n	Half-Life in Hours	Velocity Constants		
										First	Second	Third
1	34.30	109	None	0	34.30	37.04		100.0	18		0.00156 initial	0.0001719 initial
2	34.30	100	Atmos. of CO ₂	0		25.94		(100.0)	170	0.0041	0.0001989	0.0000182
5a	47.69	100	Atmos. of O ₂	0					~ 32	0.0041 last		
5b	47.69	100	5 M % Air	0					~ 32	0.033 last		
			Ascaridole									
			5 M % C ₃ H ₇ CHO	0								
3	47.69	100	None	0	43.80	45.00	2.5	91.9	87	0.00526 last	0.003726 initial	0.0001795 initial
4	47.69	100	5 M % Thiophenol	0	39.7	40.35	1.5	83.2	116	0.0043	0.0001292	
6	47.69	100	5 M % Ascaridole	0	47.69		1-2	(100.0)	30			
10	48.70	100	5 M % Thiophenol	25	42.45	43.8	3.2	96.8	16	0.0476	0.000994	0.0000839
11	47.69	100	None	25	40.3	41.3	2.5	84.5	4		0.00865	0.00042
			Nat. per.									
14	67.47	50	5 M % Thiophenol	25	32.13	32.66	1.6	95.2	21	0.02035	0.0004167	0.00005275
15	69.84	50	2 M % Ascaridole	25	31.35	31.49	0.5	89.8	16		0.00277 initial	0.000227
8	48.70	140	5 M % Thiophenol	25	41.7	63.6	52.5	85.6	5	0.1449		
7	47.69	140	None	25	47.69	66.7	40.0	(100.0)	0.4		0.0752 Initial	
			Nat. per.									
9	48.70	104	5 M % Thiophenol	25	42.20	48.35	14.3	86.6	6.7	0.1034	0.00228	0.0001051

proximate fit for a part of the reaction was found the rate constant derived from this section of the curve is given in Table 1. There is little significance to be attached, at present, to these rate constants. They are used here only as a basis for comparing the effect of catalysts.

Effect of Peroxides on the Rearrangement of Camphene Hydrochloride

The rates of rearrangement of camphene hydrochloride in the presence of peroxides and of antioxidants were compared in two experiments at 25°C. The rearrangement in ligroin is inconveniently slow at 25°C. The reaction was followed through only a small per cent rearrangement during the course of a week. Concentrations of camphene hydrochloride in per cent at the times indicated are listed in Table 2. These data give an indication of the relative rates of addition and rearrangement.

TABLE 2
REARRANGEMENT OF CAMPHENE HYDROCHLORIDE

Expt. No.	Catalyst	0 Hours	3 Hours	10 Hours	60 Hours	125 Hours
12.....	5 M % Thiophenol	75	80	84	87	85
13.....	5 M % Ascaridole	75	80	79	76	74

The reactions were not followed over a sufficient range for the conclusion to be made that the catalysts were completely without effect. It can be said with certainty, however, that there is no marked effect produced by thiophenol or ascaridole. The difference in concentrations of approximately 10 per cent or more at 125 hours is to be attributed to the reaction between hydrogen chloride and ascaridole.

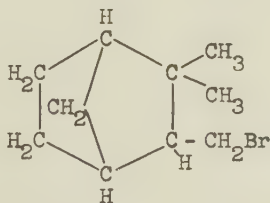
DISCUSSION OF RESULTS

Addition of Hydrogen Bromide to Camphene

In the presence of even the very small traces of peroxides which are formed in camphene solutions on standing in air, the rate of addition of hydrogen bromide is greatly increased. In the

presence of ascaridole the initial yield of camphene hydrobromide is not as high, since some hydrogen bromide adds to ascaridole. In the presence of thiophenol, an antioxidant, the rate of rearrangement is slower, but the rate of addition of hydrogen bromide is also slower. As a result, in an antioxidant experiment there is initially a little higher per cent of free hydrogen bromide than in a peroxide experiment where equal amounts of hydrogen bromide were originally added.

From results of preliminary experiments and from the study of the rate of rearrangement of camphene hydrobromide, no evidence has been found for the formation of the primary, 3'-brom isocamphene.



The presence of this compound would normally be expected to result from the addition of hydrogen bromide to camphene in the presence of peroxides. On the contrary, the optimum conditions for obtaining camphene hydrobromide are at a low temperature, 0°C. or lower, where the rate of rearrangement is slow, and in the presence of traces of peroxides which increase the rate of addition of hydrogen bromide.

It is true, however, that the presence of this primary bromide could have been completely missed in analysis if its bromine atom is alcoholyzed with an ease equal to that of camphene hydrobromide or to that of isobornyl bromide.

Effect of Peroxides on the Rate of Rearrangement

To facilitate comparison, those experiments listed in Table 1 which were carried out under identical conditions, save for the catalyst added, are grouped together in Table 3.

It is interesting to note that the greater differences in rates of rearrangement between comparable peroxide and antioxidant experiments, as indicated by the half-lives, are produced in the presence of the greater amounts of free hydrogen bromide. This

TABLE 3

Expt. No.	Camphene m M	HBr M %	Catalyst Added	Temp. Deg. C.	C. HBr ^o	TABr ^o	% Free HBr	% Add'n	Half-Life in Hours	Ratio of Half-Lives
3	47.69	100	None	0	43.80	45.00	2.5	91.9	87	1.3
4	47.69	100	5 M % Thiophenol	0	39.7	40.35	1.5	83.2	116	
6	47.69	100	5 M % Ascaridole	0			1-2	(100.0)	30	
10	48.70	100	5 M % Thiophenol	25	42.45	43.8	3.2	96.8	16	4.0
11	47.69	100	None Nat. Per.	25	40.3	41.3	2.5	84.5	4	
14	67.47	50	5 M % Thiophenol	25	32.13	32.66	1.6	95.2	21	1.3
15	69.84	50	2 M % Ascaridole	25	31.35	31.49	0.5	89.8	16	
8	48.70	140	5 M % Thiophenol	25	41.7	63.6	52.5	85.6	5	12.5
7	47.69	140	None Nat. Per.	25	47.69	66.7	40.0	(100.0)	0.4	

is taken as further substantiation for the view that peroxide catalysis takes place through free hydrogen bromide and not through the unsaturated compound¹ or the formed bromide.

By comparing the ratios of the half-lives under antioxidant and peroxide conditions in otherwise comparable experiments, it is noted that the ratio appears to be greater at 25°C. than at 0°C. This statement is only qualitatively true; for it to be exact, equal concentrations of free hydrogen bromide must occur in the compared cases. The observation that, for this limited temperature range, a rise in temperature increases the rate of rearrangement under peroxide conditions more than under antioxidant conditions is only tentative. In any case, the effect of temperature on the rates of rearrangement under the two sets of conditions is subordinate to the effect of free hydrogen bromide.

The tremendous effect of free hydrogen bromide in the presence of peroxides on the rate of rearrangement is clearly demonstrated in Experiments 11, 15, and 7, by comparing the half-lives of the reactions with the percentages of hydrogen bromide initially present.

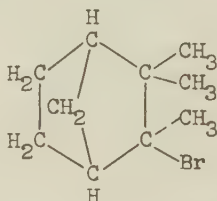
As has already been stated, the kinetic relationships between the concentrations of the substances involved in the rearrangement has not been found. Yet, from the plots made in the attempt to find the concentrations of camphene hydrobromide and hydrogen bromide at zero-time for each experiment, certain information has been gained. The initial rate for the rearrangement for a given experiment under antioxidant conditions is best expressed as a first-order reaction. For those experiments in which the camphene solutions had no oxidizing power toward ferrous ion, the initial rate is best represented as a second- or third-order reaction. This was also found to be true for those experiments in which the stock camphene solution had acquired oxidizing power toward ferrous ion by standing in air. Thus the conclusion is drawn that freshly prepared camphene-ligroin solution, which has no oxidizing power toward ferrous ion, contains sufficient quantities of peroxides to markedly affect the rate of rearrangement of camphene hydrobromide.

The initial rate of those rearrangements carried out in the presence of ascaridole cannot be expressed as any of the type

¹Cf. Experiments 14 and 15, Table 3.

reactions.

The rate constants, calculated for a first-order reaction, for a given antioxidant experiment rapidly become smaller as the rearrangement proceeds. This is due, in part, to the formation of camphene hydrobromide from isobornyl bromide by the reverse rearrangement. It is also due, in part, to the gradual loss of free hydrogen bromide, the catalyst for the rearrangement, by addition to the unreacted camphene. The apparent rate of rearrangement would be decreased by the formation of the stereoisomeric, methyl camphenilyl bromide



This tertiary bromide could be formed from camphene hydrobromide by ionization and readdition of bromide ion or more simply, by the racemization of camphene hydrobromide. From structural considerations (discussed under "Previous Work") methyl camphenilyl bromide might not be expected to rearrange. Yet its concentration in a reaction mixture would be included in the figure, found by analysis, for camphene hydrobromide since the bromine atoms of the two compounds would be expected to be alcoholized with about the same ease.

In seeking the mechanism for the rearrangement it would be very interesting to determine whether or not this stereoisomer of camphene hydrobromide is formed. Information obtained from these data concerning the formation of methyl camphenilyl bromide, unfortunately, must await the kinetic evaluation of the two influences cited which decrease the rate of the rearrangement.

Effect of an Atmosphere of Oxygen on Rate of Rearrangement

In Table 4 are relisted the data of Experiments 2 and 5 of Table 1. The concentrations of free hydrogen bromide in Experiment 2 were too small to be determined by the analytical method employed. The half-life of the reaction calculated on the basis of the initial total active bromide concentration is, however,

comparatively large. Thus it is concluded that the presence of an atmosphere of oxygen increased both the rate of addition and rate of rearrangement as long as free hydrogen bromide was present but had no effect on camphene hydrobromide as such.

TABLE 4

EFFECT OF OXYGEN ON RATE OF REARRANGEMENT AT 0°C.

Expt. No.	Cam-phene m M	HBr M %	Added Catalyst	TABr ^o	Free HBr %	Half- life	1st Order Constant
2	34.30	100.0	None Atmos. O ₂	25.94	Very small	170	0.00408 (not initial)
5a	47.69	100.0	5 M % Ascaridole in air	m M C. HBr 140.5 Hrs. 161.5 hrs.		~ 32	0.0041
				13.0	12.0		
5b	47.69	100.0	5 M % C ₃ H ₇ CHO	13.0	6.5	~ 32	0.033

The reaction vessel of Experiment 5a was cracked at the beginning of the reaction. Its contents were transferred to another container and the rearrangement followed by pipetting samples for analysis. By this procedure a large portion of the free hydrogen bromide was lost before zero-time. The half-life quoted gives an indication of the initial rapid reaction in the presence of added peroxide and free hydrogen bromide. The first-order constant quoted for the last of the reaction gives indication of the slow rate of rearrangement following the loss of the peroxide by reaction and the loss of free hydrogen bromide by faulty procedure. This experiment would have ordinarily been discarded except for the fact Experiment 5b was carried out at the same time with the same materials and, therefore, affords a striking comparison.

The rearrangement of 5b was allowed to take place in a sealed bombtube for 140.5 hours after which time it was opened for analysis. After the reaction mixture had stood in the presence of air for a day the second analysis was made.

The very marked influence of air on the rate of rearrangement in the presence of butyraldehyde indicated by an eightfold increase in rate constant is further evidence that oxygen has no

effect on camphene hydrobromide but that peroxides or an oxygen-carrier along with free hydrogen bromide must be present in order that an effect be observed.

Effect of Free Hydrogen Bromide in the Presence of an Antioxidant

The effect of the presence of hydrogen bromide with peroxides on the rate of rearrangement has been discussed. Free hydrogen bromide in the presence of an antioxidant also has a marked effect on the rate of rearrangement but not as great an effect as in the presence of peroxides. As has been noted, the initial rate of the rearrangement under antioxidant conditions is best expressed as a first-order reaction. Table 5 contains a list of the antioxidant experiments at 25°C. with the initial rate constants calculated on the basis of a first-order reaction.

TABLE 5
EFFECT OF FREE HYDROGEN BROMIDE IN THE
PRESENCE OF AN ANTIOXIDANT

Expt. No.	Camphene m M	HBr M %	C. HBr	TABr ^o	Free HBr %	% Add'n	Half-life (Hrs.)	First-Order Rate K
14	67.47	50	32.13	32.66	1.6	95.2	21	0.02035
10	48.70	100	42.45	43.8	3.2	96.8	16	0.0476
9	48.70	104	42.20	48.35	14.3	86.6	6.7	0.1034
8	48.70	140	41.7	63.6	52.5	85.6	5	0.1449

In Figure 1, Curve A, the rate constants in Table 5 are plotted against the initial concentrations of hydrogen bromide. It is noted that the curve rises very rapidly with increasing amounts of hydrogen bromide and then flattens considerably at a concentration of something over 50 M per cent.

In order to find by extrapolation what the initial rate of rearrangement would be at zero concentration of hydrogen bromide the rate constants were plotted against the concentrations of hydrogen bromide raised to a number of different powers. None of the simple functions, $1/2$, 1 , $3/2$, 2 , or $5/2$, give a straight-line relationship.

The function of the hydrogen bromide concentration giving a line of least curvature of the functions tried is k versus $\log$

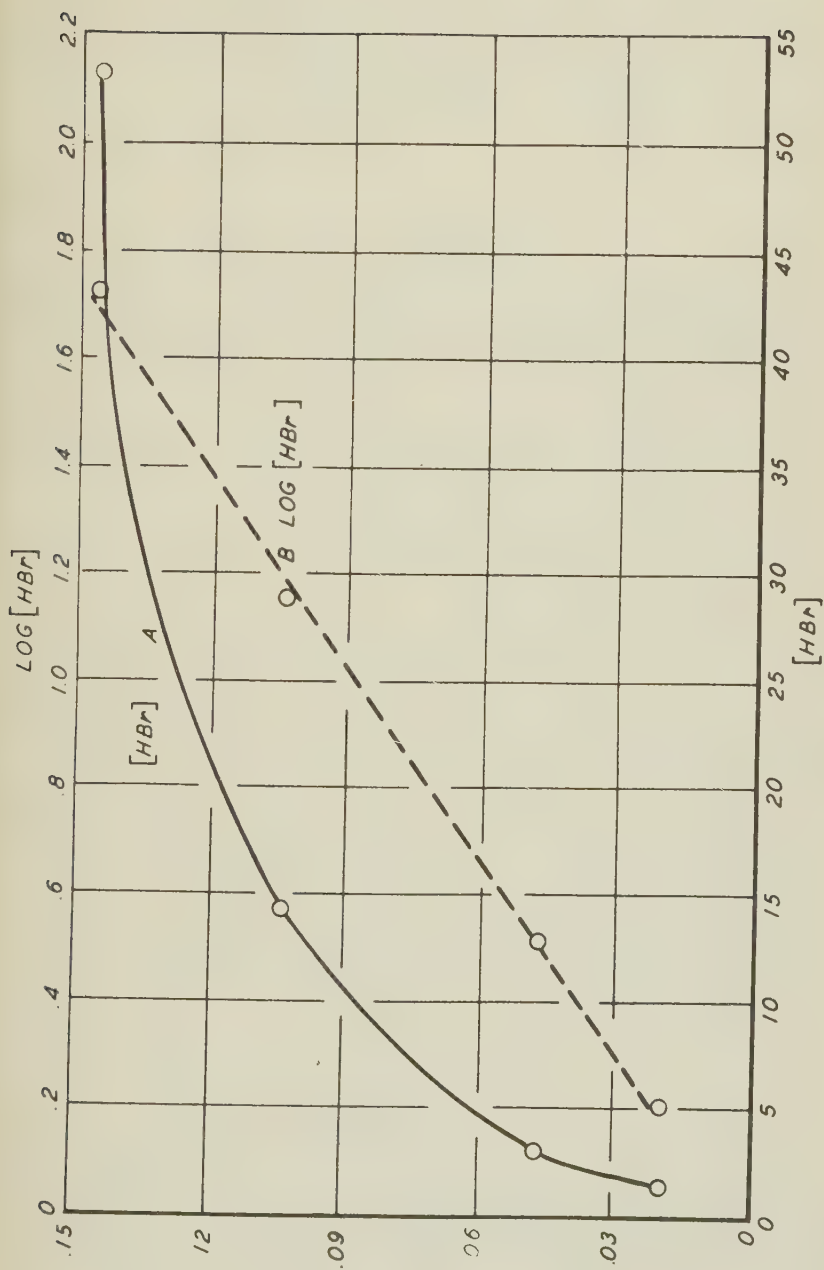


FIGURE 1.

(HBr) represented in Figure 1 by Curve B. The extrapolation of Curve 2 to zero concentration of hydrogen bromide is, of course, impossible. It can be concluded with certainty, however, that the rate of rearrangement of camphene hydrobromide in the absence of hydrogen bromide is very small if not zero.

SUMMARY

A brief review of the chemical literature relating to the rearrangement of the esters of camphene hydrate, especially that of camphene hydrochloride and camphene hydrobromide, has been given.

The effect of peroxides on the addition of hydrogen bromide to camphene and on the rate of rearrangement of camphene hydrobromide in ligroin, as the solvent, has been studied. Both the rate of addition of hydrogen bromide and the rate of rearrangement of camphene hydrobromide were found to be increased by the presence of peroxides.

The rate of rearrangement was found to be very sensitive to the concentration of free hydrogen bromide. It was concluded that in the absence of hydrogen bromide the rearrangement would not take place. This view is in agreement with that put forward by Bartlett and Pockel concerning the rearrangement of camphene hydrochloride.

The catalytic effect of free hydrogen bromide on the rate of rearrangement was found to be greater in the presence of peroxides than in the presence of an antioxidant.

The presence of peroxides has not been found to produce an effect on the addition of hydrogen chloride to camphene or on the rearrangement of camphene hydrochloride.

EXPERIMENTAL PART

Apparatus and Procedure

The apparatus for the experiments at 0°C. is shown in Figure 2. The vacuum system (not shown) consisted of a three-stage mercury pump backed by a Cenco Hyvac oil pump connected to the apparatus through a trap held at the temperature of liquid

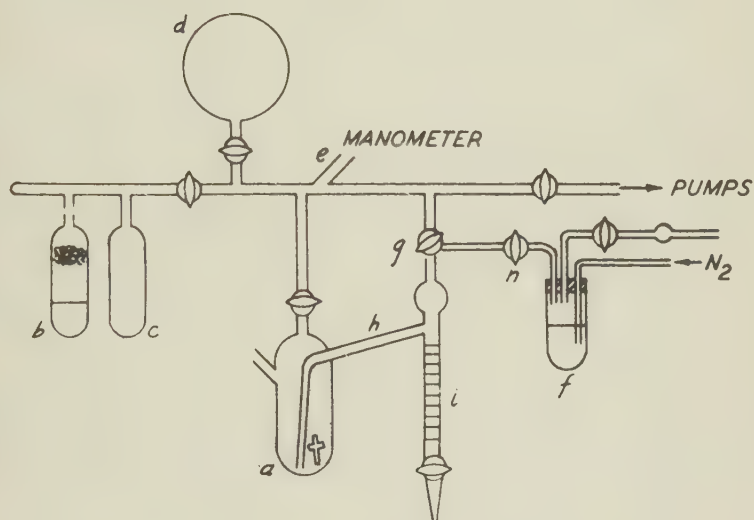


FIGURE 2.

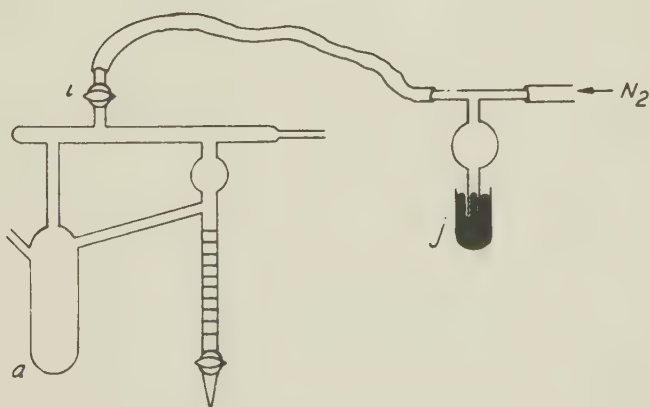


FIGURE 3.

nitrogen. The details of the apparatus will be given along with a description of the procedure in the following.

The apparatus represented by Figure 2 was thoroughly dried by continued flaming and the air displaced by dry, oxygen-free nitrogen before each experiment was begun.

The reaction vessel a, was of about 140 cc. capacity. A portion of standard camphene stock solution, usually 10 or 15 cc. containing 0.03 to 0.06 mols of camphene, was introduced into the reaction vessel through the side arm. Sufficient high boiling ligroin was then added to make the total volume of the mixture 100 cc. The liquid measurements were made at 0°C. by means of pipettes surrounded by jackets containing ice and water. The catalyst, as thiophenol or ascaridole, was then introduced. The volume of the catalyst, usually 0.1 - 0.4 cc. was neglected, that is, the total volume was still considered as 100 cc. When larger quantities of catalyst were used the volume of the ligroin added was so adjusted that the total volume of the reaction mixture was 100 cc. After the side arm had been tightly closed by means of a cork stopper, the reaction mixture was allowed to solidify in a bath of liquid nitrogen.

A tube b, containing 4 to 6 gr. of solid hydrogen bromide, 1 gr. of phosphorus pentoxide, and a loosely fitting plug of glass wool was sealed to the apparatus in the position indicated. The pumps were turned on and as the evacuation was begun the side arm of the reaction vessel a, was sealed.

When the pressure in the system was 10^{-4} mm. of Hg or less, the hydrogen bromide was melted and the liquid distilled into tube c. After the distillation was complete tube b was sealed off. For the antioxidant experiments the camphene solution was also degassed at this time. Evacuation of the system was resumed. When the pressure was 10^{-5} mm. of Hg the calculated quantity of hydrogen bromide was measured by means of the calibrated bulb d and the manometer e, and finally condensed in the reaction tube a. The reaction mixture was then warmed as rapidly as possible to 0°C. and thoroughly stirred by means of a magnetic stirrer. The time at which the pressure in the system became constant at 0°C. was considered zero-time for the rearrangement. Cooled nitrogen gas was allowed to enter the system until the total pressure was equal to that of the atmosphere. The nitrogen was cooled by passing through trap f which contained ligroin at 0°C.

Throughout the period of the rearrangement the reaction vessel was surrounded by a crushed ice-water mixture in a liter Dewar flask.

Samples of the reaction mixture were obtained by introducing a nitrogen pressure above the reaction mixture of 10 to 20 cm. above atmospheric pressure. As this pressure was released, by means of the three-way stopcock g, through the tube h, a part of the reaction mixture flowed over into the burette i. The burette was surrounded by a jacket through which ice-water was passed. Aliquot samples for analysis were introduced directly from the burette into the titrating mixtures. During the actual removal of liquid from the burette the stopcock n was open and a steady stream of nitrogen passed through trap f to the air. Nitrogen was thus available for filling the volume of the solution removed.

During the first and second samplings in several of the experiments some hydrogen bromide was lost from the system, being blown out when the nitrogen pressure was released to the air through trap f. During the course of the experiment, approximately a week, some hydrogen bromide was also lost by reaction with the mercury of the manometer. The apparatus was also rather cumbersome. Thus a modification of the apparatus, represented in Figure 3, was used for the experiments at 25°C. Since the procedure employed was the same as that described above, only the essential differences in the apparatus will be described in the following.

The hydrogen bromide tube was attached to the apparatus by a ground-glass joint. Thus the material was degassed in its original tube and not by a distillation. The hydrogen bromide was allowed to pass into the measuring bulb through a glass spiral held at about -50°C. The reaction tube without delivery tube or stirrer was connected directly by a side arm to the burette. After condensation of the hydrogen bromide in the reaction vessel the section of the line to which were attached the reaction vessel and burette was sealed off. The total volume of the apparatus was 215 cc.

The reaction mixture was warmed rapidly to room temperature and made homogeneous by vigorous shaking. The apparatus was filled with nitrogen at a pressure of about 1 cm. above atmospheric pressure through a rubber tube connected to the stopcock i. The reaction tube was then placed in a thermostat held at

25°C. $\pm$ 0.1°C. A small pump was used to circulate water of the thermostat through the jacket of the burette. During the removal of liquid from the burette a stream of nitrogen was allowed to bubble through trap j. After the loss of each cubic centimeter of liquid from the burette stopcock i was momentarily opened.

Analyses

The method of analysis for the hydrogen bromide and camphene hydrobromide was that described by Meerwein.¹ For the determination of free hydrogen bromide, a 2 cc. sample was added to 15 cc. of dry ether and titrated directly with 0.2 N sodium ethylate in absolute alcohol.

Free hydrogen chloride was determined similarly.

The total active bromide was determined by adding a 2 cc. sample to 10 cc. of cooled methyl alcohol containing an excess of 0.2 N sodium ethylate. After this mixture had been allowed to stand for an hour at 0°C. the unreacted sodium ethylate was determined by titrating with 0.2 N hydrogen chloride in absolute alcohol. From the value of the total active bromide the figure for the free hydrogen bromide was subtracted, thus giving the concentration of camphene hydrobromide. The determination of camphene hydrochloride was carried out in the same way except that the titration mixture was allowed to stand for one-half hour at 25°C. Either phenolphthalein or thymol blue was used as the indicator in the antioxidant experiments. Owing to the red-brown color of reaction mixtures containing ascaridole, only thymol blue was used as the indicator in analyses of these reaction mixtures.

The determination of total halogen was made by a method similar to that of Vaughn and Nieuland.² To a solution composed of about 8 cc. of liquid ammonia, 1 cc. of dry ether, and about 0.1 gram of sodium, contained in a large test tube, a 1 cc. sample of the reaction mixture was carefully added. The mixture was well stirred. After it had been allowed to stand for one hour at the temperature of liquid ammonia the excess sodium was neutralized by the addition of ammonium nitrate. The ammonia was then

¹Meerwein, Ann., **453**, 37 (1927).

²Vaughn and Nieuland, Ind. and Eng. Chem. Anal. Ed., **3**, 274-75 (1931).

allowed to evaporate. The remaining solid mixture was taken up in water, acidified and the halogen determined by the Volhard method.

In all cases the total halide concentration found at the beginning was greater than at the end of an experiment. For the experiments at 25°C. this loss of hydrogen bromide or hydrogen chloride was due to the diffusion of gas into the space above the liquid reaction mixture. As samples of the reaction mixture were removed this space became greater. There was also a slight loss of halogen by reaction with the stopcock grease of the two stopcocks.

For the experiments at 0°C. halogen was lost from the reaction mixture in the manner described above and also by slight reaction with the mercury in the manometer. As has been noted, from this apparatus some free hydrogen bromide was also lost from the system during sampling. Thus the total halide values for both sets of experiments serve only as a rough check on the quantity of hydrogen bromide used in each experiment.

Materials

Camphene of commercial grade obtained from du Pont was separated from impurities, in part, by filtration. The product was distilled through an eight bulb Schneider column. The fraction boiling at 156-8°C. was recrystallized two or three times from absolute methyl alcohol. Finally, the material melting sharply between 46°C and 48°C. was distilled under an atmosphere of carbon dioxide directly into a weighed volumetric flask. After the second weighing had been made, ligroin was added to the calibration mark on the flask at 0°C or 25°C. Camphene purified in this manner was peroxide free and the camphene-ligroin solution stored in a well stoppered volumetric flask remained free of peroxides for several days.

High boiling ligroin was shaken with about an equal volume of concentrated sulfuric acid, then treated with a small portion of saturated aqueous potassium permanganate, washed with water and dried over anhydrous calcium chloride. The material was then fractionated by distillation through an eight bulb Schneider column and stored over sodium wire. Ligroin boiling between 100°C-120°C. purified in this way was free of peroxides and of unsatu-

rated compounds.

Hydrogen bromide was prepared by dropping bromine into boiling tetralin. The gas was passed through a trap held at about -50°C . and then through two absorption tubes, the first containing red phosphorus and the second phosphorus pentoxide. The hydrogen bromide from this apparatus was collected directly in tube b, referred to above.

The ascaridole used was the C. P. product obtained from the Eastman Kodak Company. The refractive index, n_D^{20} of the material was found to be 1.4736, which is the same as that reported by Paget.¹ The ascaridole was used without further purification.

The thiophenol was also Eastman's C. P. product. It was distilled shortly before addition to a reaction mixture.

Nitrogen gas from a commercial cylinder was passed through two wash bottles containing pyrogallol, one wash bottle containing chromous sulfate,² and finally, through a Drexel bottle containing concentrated sulfuric acid.

Data

In the determinations of free hydrogen bromide and total active bromide duplicate samples were taken for each analysis. In general, good checks for the free hydrogen bromide content were obtained. These values are considered accurate to the first decimal place. The variation in values of total active bromide was usually not greater than two parts in the first decimal place.

Analyses for the total halide content of the reaction mixture were usually made shortly after zero-time and at the close of the experiment. Where checks in duplicate analyses were not obtained a notation is made.

The quantity of catalyst added was calculated on the basis of the amount of camphene hydrobromide that would have been formed in the reaction mixture on the assumption of 100 per cent addition of the hydrogen bromide.

Time is reported throughout in hours.

¹Paget, Analyst, 51, 170-76 (1926).

²The chromous sulfate solution was prepared by the method of Stone, J. Am. Chem. Soc., 58, 2591 (1936).

Expt. 1				Expt. 2			
34.30 mM Camphene 1.1 M O°C . Reagents Pure Atmosphere of CO_2				34.30 mM Camphene 1.0 M HBr O°C . Atmosphere of O_2 Natural Peroxides			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
2.08	3.36	33.92	36.70	2.62	0.02	25.89	a)
13.83	2.90	22.20		18.88	0.00	22.54	28.39
24.92	2.92	17.43		43.25	0.00	20.99	
36.87	2.92	14.68		70.83	0.00	19.51	
96.00	2.22	9.83		93.87	0.00	17.73	
162.67	2.78	9.28	35.59	141.22	0.00	14.61	
Expt. 3				Expt. 4			
47.69 mM Camphene 1.0 M HBr O°C . Reagents Pure Atmosphere of N_2				47.69 mM Camphene 1.0 M HBr O°C . 5 M % Thiophenol Atmosphere of N_2			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.82	1.25	44.45		0.58	0.52	40.32	42.49
20.40	0.62	34.26		12.95	0.12	34.88	
43.33	0.62	28.34	47.04 ^b	33.00	0.12	33.75	
73.10	0.42	23.91		59.80	0.12	30.49	
92.70	0.42	21.55		87.27	0.10	27.50	
117.15	0.21	18.90		110.82	0.10	24.59	41.86
140.92	0.42	17.00	45.73 ^b	129.40	0.04	22.40	

^aFree HBr lost during sampling.

^bNot checked.

Expt. 5a				Expt. 5b			
47.69 mM Camphene 1.0 M HBr 0°C. 5 M % Ascaridole				47.69 m M Camphene 1.0 M HBr 0°C. 5 M % Butyraldehyde			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.89	0.42	36.65	44.31	142.13	0.42	12.78	45.36
41.32	0.04	20.11		161.84	0.19	6.63	
63.72	0.02	17.06					
137.75	0.04	13.28	43.29				
159.18	0.02	11.98					
Expt. 6				Expt. 7			
47.69 m M Camphene 1.0 M HBr 0°C. 5 M % Ascaridole Atmosphere of O ₂				47.69 m M Camphene 1.4 M HBr 25°C. Natural Peroxides Atmosphere of N ₂			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.37	0.64	38.21	45.75	0.50	14.48	33.59	60.74
25.37	0.19	25.21		2.08	14.85	20.67	
53.17	0.09	21.63		3.85	14.97	18.13	
73.62	0.05	19.73		5.20	15.15	17.26	
96.50	0.04	17.95		7.70	14.83	16.06	59.45
125.37	0.04	16.78					
144.23	0.04	15.80	44.77 ^a				

^aNot checked.

Expt. 8				Expt. 9			
48.70 m M Camphene 1.4 M HBr 25°C. 5 M % Thiophenol Atmosphere of N ₂				48.54 m M Camphene 1.04 M HBr 25°C. 5 M % Thiophenol Atmosphere of N ₂			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.03	21.28	62.87		0.12	4.77	47.01	
0.38	18.56	58.66	63.42 ^b	0.92	4.27	42.82	50.52
0.90	18.63	55.25		2.48	3.02	35.62	
3.42	18.66	44.14		4.77	2.90	28.60	
5.82	18.39 ^a	38.17		6.43	3.31	24.95	
7.47	18.02	33.22	62.54 ^b	9.90	2.43	19.43	
9.23	17.08	27.07		22.90	2.98	10.40	
....				35.00	2.37	8.10	
....				72.87	2.66	6.55	

Expt. 10				Expt. 11			
48.70 m M Camphene 1.0 M HBr 25°C. 5 M % Thiophenol Atmosphere of N ₂				47.69 m M Camphene 1.0 M HBr 25°C. Natural Peroxides Atmosphere of N ₂			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.27	2.42	43.35		0.12	1.92	40.60	
1.72	2.07	41.74	48.48 ^b	0.47	1.59	36.41	
3.43	1.84	37.63		1.37	1.34	30.22	
5.72	1.60	33.64		3.30	1.11	22.67	
8.93	1.50	29.64		6.68	1.03	17.93	
23.22	1.28	18.02		19.05	0.97	11.96	
49.08	0.99	8.86		47.22	0.92	9.91	
72.57	0.78	5.38		69.73	0.90	9.46	
94.10	0.75	4.81		93.55	0.86	8.97	

^aStopcock on burette was broken off at 3.5 hours. It was reconnected by means of a rubber tube.

^bValues not checked.

Expt. 12				Expt. 13			
47.69 m M Camphene 1.0 M HCl 25°C. 5 M % Ascaridole Atmosphere of N ₂				48.70 m M Camphene 1.0 M HCl 25°C. 5 M % Thiophenol Atmosphere of N ₂			
Time	Free HCl	TACl	Total Chloride	Time	Free HCl	TACl	Total Chloride
0.13	7.25	43.01		0.25	9.04	46.22	
2.20	3.06	40.01		1.48	7.72	46.04	
10.33	1.84	39.55		5.70	6.25	46.20	
21.57	1.69	38.36		24.38	4.64	46.83	
47.70	1.52	36.52		58.97	4.02	46.44	
71.52	1.38	37.63		77.14	3.66	46.05	
97.52	1.26	36.98	44.07	97.25	3.46	45.74	47.25 ^a
121.13	1.10	36.26		125.04	3.20	45.39	
.....				147.24	3.06	44.24	

Expt. 14				Expt. 15			
67.47 m M Camphene 0.5 M HBr 25°C. 5 M % Thiophenol Atmosphere of N ₂				69.84 m M Camphene 0.5 M HBr 25°C. 2 M % Ascaridole Atmosphere of N ₂			
Time	Free HBr	TABr	Total Bromide	Time	Free HBr	TABr	Total Bromide
0.15	0.51	32.57		0.08	0.05	31.48	34.59
1.75	0.50	31.38	33.52 ^a	1.45	0.04	27.67	
4.25	0.41	28.71		2.97	0.04	25.07	
9.43	0.41	23.62		6.37	0.01	21.75	
21.97	0.36	17.13		9.57	<0.01	19.88	
46.77	0.18	9.92		21.47	<0.01	14.14	
74.68	0.08	6.01		45.25	<0.01	8.10	
97.75	0.03	4.55	33.41 ^a	72.08	<0.01	4.76	
121.12	0.03	3.52		96.80	<0.01	3.21	
.....				120.00	<0.01	2.06	

^aValue not checked.

